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The crystal structure and thermotropic liquid-crystal properties of *N*-*n*-undecyl-D-gluconamide

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ABSTRACT

N-*n*-Undecyl-D-gluconamide, $C_{17}H_{35}O_6$, crystallizes in space group $P1$, with one molecule in a unit cell $a = 5.2267(6), b = 19.628(9), c = 4.7810(4)$ Å, $\alpha = 93.23(2), \beta = 95.60(1), \gamma = 89.58(2)°$, $V = 487.35$ Å^3, $D_x = 1.19$ g.cm^{-3}. The crystal lattice is isostructural with *N*-*n*-heptyl-D-gluconamide having monolayer head-to-tail molecular packing. The molecules have a V-shaped conformation. The hydrogen bonding of the gluconamide moieties includes a four-link homodromic cycle. The transition to a smectic A liquid-crystal phase at 156.7° is preceded by two crystal-to-crystal phase transitions at 77.2° and 99.4°. The long *d*-spacing of the intermediate crystal phase of 39 Å, and the *d*-spacing of the liquid-crystal phase of 32 Å, are consistent with a transition to a bilayer head-to-head molecular packing.

INTRODUCTION

The discovery that octyl β-D-glucopyranoside is an effective nonionic surfactant for solubilizing and crystallizing membrane proteins[1] prompted the synthesis of a variety of long-chain alkylated carbohydrates. These include other *n*-alkyl *O*- and *S*-glucopyranosides[2–4], octyl and dodecyl lactoside, dodecyl cellobioside, and dodecyl maltoside[5,6]. Molecules having long-chain alkyl groups linked to open-chain carbohydrates have also been synthesized. These include the *N*-*n*-alkyl-D-ribonamides and D-gluconamides[7–9] and the 1-deoxy-1-(*N*-methylalkanamido)-D-glucitols[10,11]. Crystal structure analyses have been reported for the *N*-*n*-heptyl-, -*n*-octyl-, and -*n*-decyl-D-gluconamides[12,13] (**1**) and the 1-deoxy-1-(*N*-methyl-octanamido, -nonanamido, and -undecanamido)-D-glucitols[14,15] (**2**)*.

1 $CH_3{\cdot}(CH_2)_n{\cdot}NH{\cdot}CO{\cdot}(CHOH)_4CH_2OH$; $n = 6, 7, 9$
2 $CH_3{\cdot}(CH_2)_n{\cdot}CO{\cdot}N(CH_3){\cdot}CH_2(CHOH)_4CH_2OH$; $n = 6, 7, 9$

All these compounds form thermotropic liquid crystals. A study of the thermotropic properties of the *N*-alkyl gluconamides indicated that the liquid-crystal phases are smectic A, with a bilayer structure and interdigitizing alkyl chains[16]. The more soluble

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* Also named *N*-D-gluco-*N*-methyl alkanamides[10], alkanoyl-*N*-methyl glucamides[14], and *N*-(1-deoxy-D-glucitol-1-yl) alkanamides.

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compounds, such as the alkyl β-glucopyranosides, can form a succession of lyotropic liquid-crystal phases, analogous to those of the soaps[17].

The *N*-alkyl gluconamides are not soluble enough to be useful as surfactants, but they do form, on cooling from hot solutions, gels which show helical rope-like structures under the electron microscope[18].

As in the long-chain fatty acids, compounds with even and odd numbers of carbon atoms in the alkyl chains form different crystal structures[19]. In the *N*-alkyl gluconamides (**1**) the molecular packing is the same irrespective of whether the alkyl chains are odd or even. This is a monolayer packing with head-to-tail arrangement of the layers. Among the 1-deoxy-1-(*N*-methylalkanamido)-D-glucitols (**2**) only the compounds with an odd number of carbon atoms in the alkyl chains have the head-to-tail monolayer molecular packing. With the even numbered alkyl chains, the molecular packing is the more common bilayer head-to-head pattern which is observed in all the *n*-alkyl pyranosides hitherto studied and in related structures such as cholesteryl myristate and the triacetyl- and glycosyl-phytosphingosines[20].

In this paper, we report the crystal structure of another member of series **1** and discuss its thermotropic transitions.

EXPERIMENTAL

Crystals were obtained from Dr. B. Pfannemüller, Institut für Macromolekulare Chemie, Hermann-Staudinger-Haus, Universität Freiburg, F.R.G. The crystal structure determination and structure refinement data are given in Table I. The atomic parameters of the hydrogen atoms on the alkyl chain were generated assuming C–H = 1.0 Å and valence angles of 109.5°, with isotropic *B*-values 20 percent larger than the carbon atom to which they are attached. All other hydrogen atoms were located on difference Fourier syntheses. The positional and thermal parameters were refined only

TABLE I

Crystal data and X-ray diffraction structure-analysis data for *N*-*n*-undecyl-D-gluconamide at 25°

Crystal data

$C_{17}H_{35}NO_6$; mol. wt. 349.4; m.p. 156.7°; c.p. 190.0°; $P1$; $Z = 1$
Cell dimensions, $a = 5.2267(6)$, $b = 19.628(9)$, $c = 4.7810(4)$ Å, $\alpha = 93.23(2)$,
$\beta = 95.60(1)$, $\gamma = 89.58(2)°$
$V = 487.35$ Å^3; $D_x = 1.19$ g·cm^3

Structure determination and refinement data

Crystal dimensions, 0.75 × 0.3 × 0.03 mm
Radiation Cu$K\alpha$ ($\lambda = 1.5418$ Å), Ni-filtered; $\mu_{Cu} = 0.74$ cm^{-1}
1739 intensities measured on a CAD-4 diffractometer; 1450 with $I_0 > 2\sigma(I)$
Absorption corrections were applied
Structure solved using MITHRIL[21] on 302 E values > 1.25 to generate 109 quartets of which 97 were negative
Refinement using UPALS[22] on $R = \Sigma\omega(|F_o|-|kF_c|)^2/\Sigma\omega F_o|^2$, where $\omega = \sigma^{-2}(F_c)$
Final refinement values, $R = 0.040$; $R_w = 0.041$; $S = 1.58$, for 1450 reflections for which $I > \sigma(I)$

TABLE II

Atomic positional parameters and equivalent isotropic thermal parameters for *N*-*n*-undecyl-D-gluconamide

Atom	x/a	y/b	z/c	U_{eq} *or* U_{iso} ($\AA^2$)[a]
O-1	2427(7) × 10^{-4}	7620(2) × 10^{-4}	−1883(8) × 10^{-4}	680(9) × 10^{-4}
O-2	−1920(6)	8506(2)	2320(7)	514(7)
O-3	−681(6)	9194(2)	−2245(7)	430(6)
O-4	215(6)	9913(2)	3300(7)	453(7)
O-5	5103(6)	9983(2)	−1458(7)	466(7)
O-6	5985(6)	10708(2)	4045(7)	464(7)
N	−1848(0)	7518(0)	−1597(0)	512(9)
C-1	459(8)	7793(2)	−876(8)	481(10)
C-2	540(8)	8401(2)	1293(8)	436(9)
C-3	1363(7)	9025(2)	−164(7)	407(8)
C-4	2207(7)	9643(2)	1743(7)	384(8)
C-5	3077(7)	10234(2)	104(8)	407(9)
C-6	3934(8)	10851(2)	1972(8)	472(9)
C-7	−2297(8)	6960(2)	−3735(9)	635(12)
C-8	−2497(9)	6274(2)	−2463(10)	655(12)
C-9	11(8)	6010(3)	−1118(11)	679(13)
C-10	−176(9)	5320(2)	156(11)	714(14)
C-11	2340(9)	5032(3)	1362(11)	726(14)
C-12	2126(10)	4355(3)	2670(12)	764(15)
C-13	4686(9)	4051(3)	3783(12)	764(15)
C-14	4473(9)	3377(3)	5118(12)	783(16)
C-15	6999(9)	3060(3)	6185(12)	783(16)
C-16	6762(11)	2389(3)	7480(16)	988(21)
C-17	9246(11)	2060(3)	8459(17)	1095(25)
H-20	−120(8) × 10^{-3}	900(2) × 10^{-3}	268(9) × 10^{-3}	63 × 10^{-3}
H-30	−187(9)	934(2)	−176(10)	63
H-40	9(10)	967(2)	482(11)	63
H-50	531(8)	1025(2)	−277(10)	63
H-60	727(8)	1045(2)	384(9)	63
H-1	−318(8)	766(2)	−81(9)	63
H-2	186	831	289	51
H-3	286	888	−126	51
H-4	370	951	307	51
H-5	160	1036	−127	51
H-6	449	1122	76	63
H-6′	245	1105	290	63
H-7	−87	694	−500	76
H-7′	−390	705	−500	76
H-8	−381	631	−109	76
H-8′	−324	593	−399	76
H-9	76	635	39	81
H-9′	133	597	−253	81
H-10	−105	498	−130	84
H-10′	−140	536	169	84
H-11	354	498	−18	86
H-11′	323	537	277	86
H-12	120	402	129	89

Continued overleaf

TABLE II (*contd.*)

Atom	x/a	y/b	z/c	U_{eq} or U_{iso}
H-12′	100	441	426	89
H-13	582	400	221	91
H-13′	561	438	518	91
H-14	350	305	369	91
H-14′	332	343	664	91
H-15	795	338	759	91
H-15′	814	300	460	91
H-16	567	245	907	114
H-16′	569	207	604	114
H-17	899	160	878	127
H-17′	1070	230	941	127
H-17″	1051	210	698	127

[a] $U_{eq} = 1/3\sum_i\sum_j U_{ij}a_i^*a_j^*\,\mathbf{a}_i\mathbf{a}_j$, from the refined, anisotropic, thermal parameters.

for those hydrogens involved in the hydrogen bonding. The atomic parameters are given in Table II[†]. Figure 1 shows the molecular conformation and the atomic notation.

The powder patterns and liquid-crystal patterns shown in Fig. 2 were taken from samples in a 0.9 mm glass capillary on a Nicolet X100A area detector with CuKα radiation at 55 kV and 200 mA from a Rigaku RU-200 rotating anode X-ray tube. The sample to detector distance was 31 cm and the exposure time was 30 to 60 s.

RESULTS AND DISCUSSION

Molecular structure. — The overall molecular conformation is V-shaped as shown in Fig. 1, with both the alkyl chain and the gluconyl moieties fully extended. The bend occurs at the amide link, with C-3–C-2–C-1–N = −116° (−114°), C-1–N–C-7–C-8 = 101° (101°), and N–C-7–C-8–C-9 = −71° (−64°). The values in parentheses are from the isostructural *N-n*-heptyl crystal[13]. There is clearly very little conformational change with increase of alkyl chain length. All other carbon-chain torsion angles are within 3.5° of 180°, except for C-4–C-3–C-2–C-1 which is −165.6°. The alkyl chain has a small curvature as shown by the C–C–C–C torsion angles, which are all a few degrees less than +180° as shown in Table III[*]. The amide torsion angle C-2–C-1–N–C-7 is +177° (176°). The fully extended carbon-chain conformation of the glucitol residue is also observed in **2** with n = 6 (MEGA-8), but not with n = 9 (MEGA-11). This conformer is considered to be the higher energy one because of the *syn* diaxial orien-

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[*] See deposited material.

[†] Lists of structure amplitudes, anisotropic temperature factors for the C, N, O atoms, and Table III, giving bond lengths, valence angles, and selected torsion angles, have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/9345/*Carbohydr. Res.*, 207 (1990) 211–219.

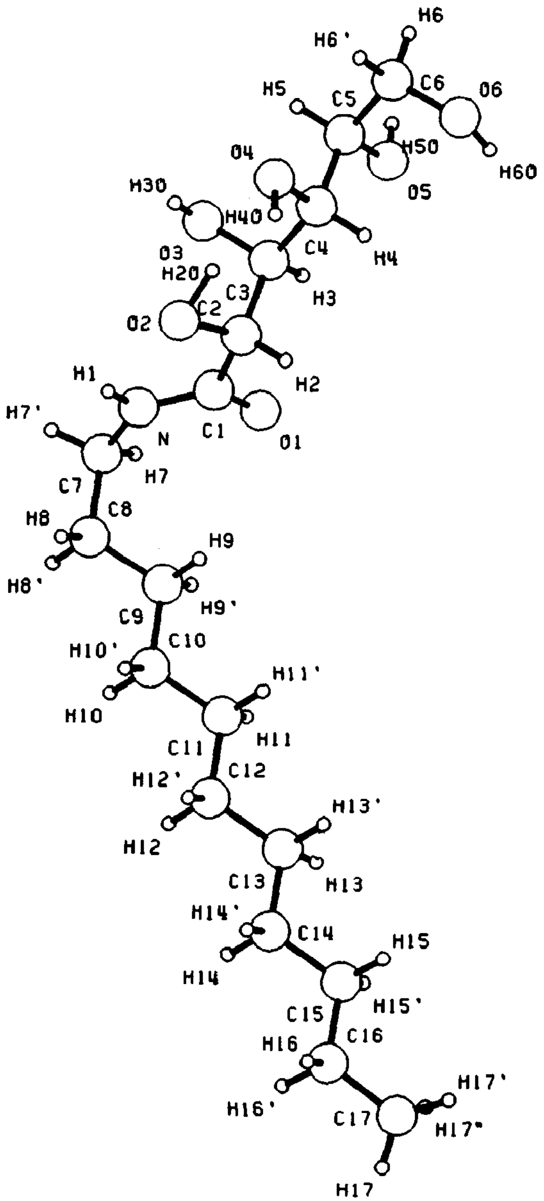

Fig. 1. Molecular conformation and atomic notation for *N*-*n*-undecyl-D-gluconamide.

tation of the C-2–OH and C-4–OH bonds[23]. As in MEGA-8 and in the A form of potassium gluconate[24], the conformation is stabilized by intramolecular hydrogen bonding between O-4-H and O-2. The orientation of the primary alcohol O-6-H bond is *gauche* to the carbon chain, with C-4–C-5–C-6–O-6 = +57.6°.

The overall length of the molecule in the conformation found in the crystal, *i.e.* the distance H-6–H-17, is 19.2 Å. The length of the molecule at maximum extension, *i.e.* with both chains nearly colinear and C-6-OH *trans* to the carbon chain, is 24.5 Å.

The C–C bond lengths in the gluconyl residue range from 1.508 to 1.532 Å with a mean value of 1.519 Å. In the alkyl chain they range from 1.503 to 1.524 Å with a mean value of 1.512 Å, with the exception of the terminal C-15–C-16 and C-16–C-17, which are 1.498 Å and 1.492 Å owing to the bond-shortening effect of thermal motion. The C–O bond lengths range from 1.420 to 1.430 Å with a mean value of 1.427 Å. The C-1 = O-1 bond length is 1.239 Å. The C-1–N peptide bond is 1.332 Å, and N–C-7 is

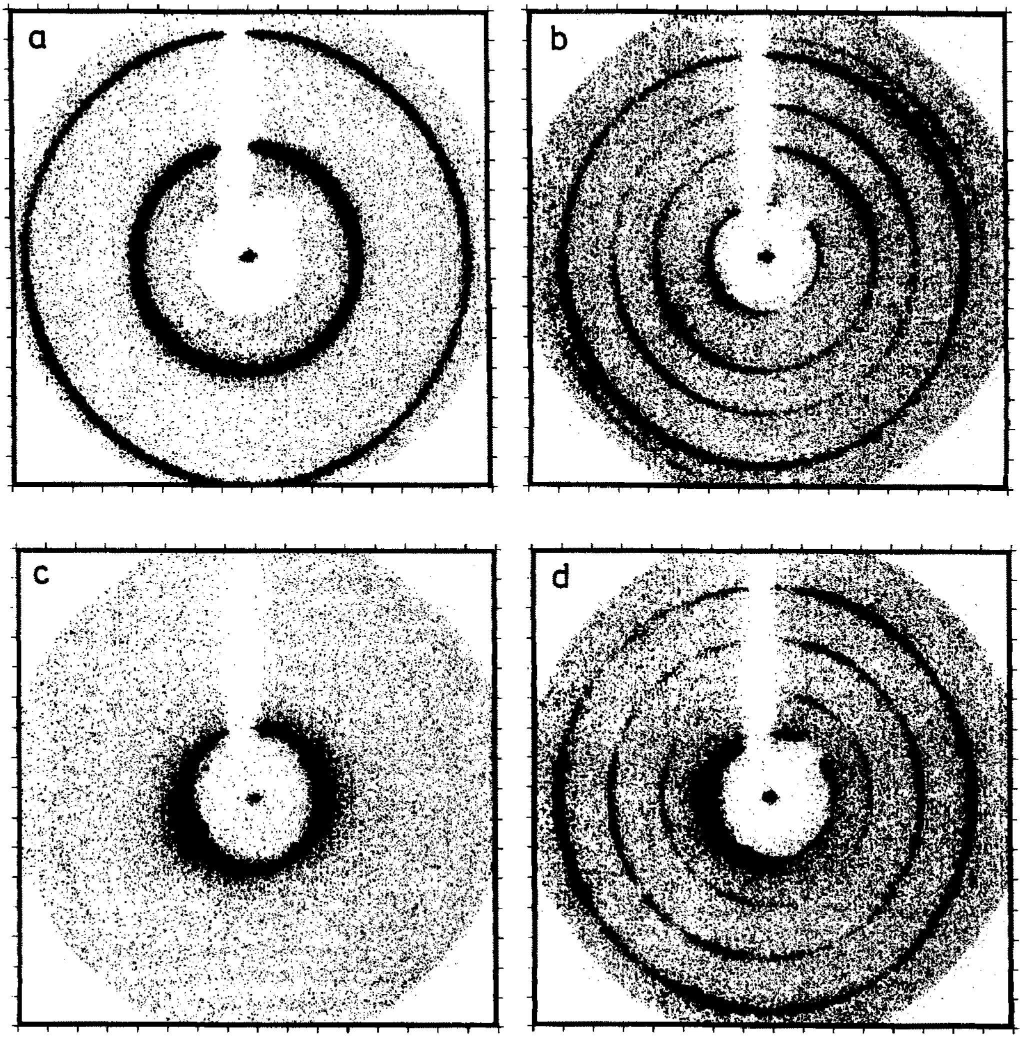

Fig. 2. X-ray diffraction patterns for *N*-*n*-undecyl-D-gluconamide: *a*, powder patterns of original material at 25° (corresponds to single crystal data); *b*, powder pattern of second crystal phase at 90°; *c*, liquid-crystal pattern after heating above 160° and cooling; *d*, powder pattern after cooling for two days and recrystallization.

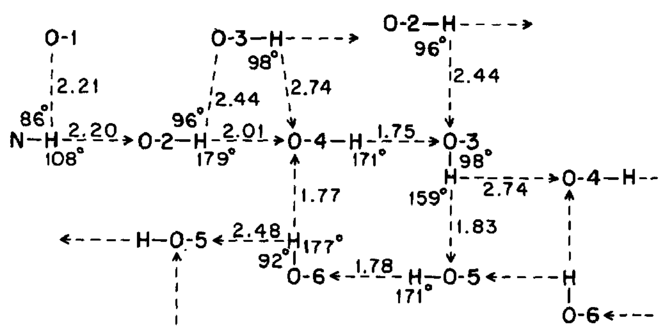

Fig. 3. Schematic of hydrogen bonding. The O–H covalent bond lengths have been normalized to 0.97 Å.

1.460 Å. The O–H bond lengths range from 0.70 to 0.88 Å, and are thus shorter than the standard neutron diffraction value of 0.97 Å because of their charge-density distribution[25].

The C–C–C valence angles range from 107.1 to 116.3° with mean of 114.8° in the gluconyl residue. In the alkyl chain they are more uniform, ranging from 114.3 to 115.4° with a mean of 114.8°. The C-1–N–C-7 angle is 123.1° and the N–C-7–C-8 angle is 112.4°.

Molecular packing and hydrogen bonding. — The molecular packing is monolayer, head-to-tail with parallel alkyl chains. It is isostructural with that reported for the *N*-*n*-heptyl homologue[13]. The same type of packing is also observed in the monoclinic crystal structure of the *n*-decyl compound (see Fig. 3 in ref. 13).

The hydrogen bonding is shown schematically in Fig. 3. The principal bonding is a four-bond *homodromic* cycle[26], linking O-4-H, O-3-H, O-5-H, and O-6-H, with hydrogen bond lengths between 1.75 and 1.83 Å and angles between 159 and 177°. These are linked by two intramolecular interactions which are the minor components of three-center bonds from O-6-H····O-5 and O-3-H····O-4. The N–H group forms a three-center bond to the carbonyl oxygen O-1, and an intramolecular bond to O-2. Oxygen O-2 is linked to the homodromic cycles through a three-center bond to O-4 and O-3, both components of which are intramolecular.

This feature of the crystal structure is common to all four *N*-alkyl gluconamide crystal structures hitherto studied, irrespective of the difference in crystal symmetry between those with odd- and even-numbered carbon atoms in the alkyl chains.

Thermotropic liquid crystal properties. — The thermotropic liquid-crystal properties of the *N*-*n*-alkyl gluconamides (1) having $n = 6$ to 12, and 18, have been described elsewhere[16]. *N*-Undecyl gluconamide has two low-enthalpy transitions, at 77.2 and 99.4° and a high-enthalpy transition to a liquid crystal at 156.7°. This changes to an isotropic liquid with some decomposition at 190°.

The X-ray diffraction patterns shown in Fig. 2 were taken at 25, 90, and 165°. The powder pattern, Fig. 2a, corresponds to the single-crystal structure having $d_{010} = 19.5$ Å and $d_{020} = 9{\cdot}8$ Å. The powder pattern at 90°, Fig. 2b, shows a different crystal structure with *d* spacings of 39.4, 20.1, 14.2 (vw), 10.8, and 9.9 (vw) Å. The lattice spacing of approximately twice the overall length of a molecule suggests that this is a crystal-to-crystal transition to a bilayer head-to-head molecular packing. The liquid-crystal pattern, shown in Fig. 2c, has a *d* spacing of 32 Å, which is also consistent with a bilayer head-to-head molecular cluster. After cooling to room temperature and recrystallization over a period of two days, the pattern in Fig. 2d was obtained. This showed that recrystallization is to the second (bilayer) crystalline phase, rather than the original monolayer crystal structure.

Our interpretation of these results is that the crystals obtained from ethanol–water solution have a monolayer head-to-tail packing stabilized by a particularly strong hydrogen-bond scheme. The same homodromic four-link cycle is responsible for the insolubility in cold water of D-galactaric acid (mucic acid)[27]. Thermal motion on heating disrupts the hydrogen bonding, and at 77° the crystals transform to a structure having the more common head-to-head bilayer packing, which is the precursor to the bilayer smectic A liquid-crystal phase. This crystal-to-crystal precursor transition occurs with all the *N*-alkyl gluconamides studied.

An interesting feature of the thermotropic transitions of the *N*-alkyl gluconamides is that the melting points are relatively constant irrespective of alkyl chain-length, ranging from 150° for the heptyl to 160° for the nonyl, while the clearing point increases regularly with increasing chain length, from 156° for heptyl to 190° for undecyl. This suggests that in the transition from crystal to liquid crystal a "core" of stacked alkyl chains is retained rather than hydrogen-bonded carbohydrate moieties as previously suggested[28]. A similar interpretation is applied to the thermotropic properties of the series of aldose dialkyl dithioacetals[29].

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